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Procedia CIRP 26 (2015) 162 – 166

www.elsevier.com/locate/procedia

12th Global Conference on Sustainable Manufacturing

Performance comparison of three common proton exchange membranes for sustainable bioenergy production in microbial fuel cell

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Abstract

Proton exchange membranes (PEMs) have essential role in the performance of microbial fuel cells (MFCs). They act as a separator and separate anode and cathode compartments and they also transfer protons between anode and cathode. In this study three types of PEMs (Nafion 112, SPEEK and Nafion 117) have been applied to MFC and the amount of produced bioenergy with the feed of a wastewater in 5000 m/l chemical oxygen demand (COD) have been reported. It has been observed that the MFC working with Nafion 117 as separator produced the highest power among the other MFCs. Also It was found that the produced power was 179.7 mW/m^2 for Nafion 117 while it was 126.1 for SPEEK and 19.7 for Nafion 112. Moreover it has been concluded that the low power production of Nafion 112 was due to the diffusion of oxygen from the cathode chamber to the anode chamber that disturb the microorganism's metabolism for degradation of organic compounds. Generally we have found a new economic PEM for using in MFCs.

Peer-review under responsibility of Assembly Technology and Factory Management/Technische Universität Berlin.
Keywords: Membrane; Wastewater, COD, Power generation, Microbial fuel cell

1. Introduction

Amid growing competition for freshwater from industry and cities, coupled with a rising world shortage of potash, nitrogen and phosphorus, an international study predicts a rapid increase in the use of treated wastewater for farming and other purposes worldwide in the other side conventional sewage and wastewater treatments require high amount of energy [1]. Drinking water and wastewater systems account for approximately 3-4 percent of energy use in the United States, adding over 45 million tons of greenhouse gases annually [2]. Water and wastewater treatment and distribution in the United States is estimated to consume 50,000 GWh, representing 1.4 percent of the total national electricity consumption. Further, drinking water and wastewater plants are typically the largest energy consumers of municipal governments, accounting for 30-40 percent of total energy consumed. In the other side the depletion of natural energy sources is an inevitable cause for concern in the modern world. Because fossil fuels can pollute the air and are exhaustible, there arose a need for renewable sources of energy that are not only cleaner but

Peer-review under responsibility of Assembly Technology and Factory Management/Technische Universität Berlin.
doi:10.1016/j.procir.2014.07.169

also more durable and also the major piece of the world's energy problem which is mostly by fossil fuel is high **price**. Prices continue to be far above from the hands of small industries[3].

Moreover, interests to find out renewable, sustainable and clean energy source with minimum or zero environmental pollution has been increased [4].One of the emerging source of renewable energy is fuel cell. Microbial fuel cell (MFC) is a type of fuel cell which converts the biochemical energy stored in organic matter by the aid of microorganism as biocatalysts [5-6]. It means that the chemical oxygen demand (COD) of wastewater decreased while producing electricity. The limitations of wide spread application of MFC as an alternative source of energy is low power output and high cost of operation for commercial applications. Power generation of MFC depends on many factors including type of membrane, catalyst, substrate, configuration, temperature etc [7].

Among these factors, the membrane of an MFC has been deemed the most important part of the whole system, as it is the membrane that separates the cathode from the anode. The membrane must support the transfer of protons from the anode to the cathode but prevent the transfer of other materials like oxygen and substrates. As if the oxygen penetrates to the anode part make the process in the anode aerobic and the power density and wastewater treatment efficiency will come down. Also penetration of media to the cathode cause the decline of power out and also it effects on the microorganisms' efficiency for COD removal [8].

Nomenclature

DS	Degree of sulfonation
Pt	Platinum
COD	Chemical Oxygen Demand
MFC	Microbial Fuel Cell

2. Materials and methods:

2.1. Synthesis of SPEEK

For the preparation of solfunated poly ether ether ketone (SPEEK), 20g of polyether ether ketone (PEEK) powder (Goodfellow Cambridge Limited, UK) was dissolved slowly in 500mL of 95-98% concentrated sulphuric acid (R & M Chemicals, Essex, UK).

This solution was stirred vigorously until the entire PEEK was dissolved completely. Next, the homogenous solution was continuously and thoroughly stirred at a controlled temperature of 80^{o}C for 4 to get the SPEEK with acceptable degree of sulfonation. The SPEEK solution was poured into a large excess of ice water to precipitate the SPEEK polymer. The solid was then collected by filtering the solution through a Whatman filter paper. Finally, the SPEEK was dried at 70^{o}C to remove any remaining water before use [9].

2.2 *Determination of DS*

The degree of sulphonation (DS) was measured by 1H Nuclear Magnetic Resonance (FT-NMR ADVANCE 111 600 MHz with Cryoprobe) spectroscopic analysis (Bruker, Karlsruhe, Germany). Before taking the measurement, the SPEEK was dissolved in dimethyl sulphoxide (DMSO-d_6). The DS can be calculated by the following equation,

$$\frac{DS}{S-2DS} = \frac{A_1}{A_2} \qquad (0 \leq \mathrm{DS} \leq 1) \qquad (1)$$

Where S is the total number of hydrogen atoms in the repeat unit of the polymer before sulphonation, which is 12 for PEEK, A_1 (H_{13}) is the peak area of the distinct signal, and A_2 is the integrated peak area of the signals corresponding to all other aromatic hydrogens. To calculate the DS percentage (DS %), the answer for the DS has to be multiplied by 100 [10].

3. Results and Discussion

The schematic of a MFC was shown in the Fig.1. The figure clearly illustrated that MFC composed of two chambers.

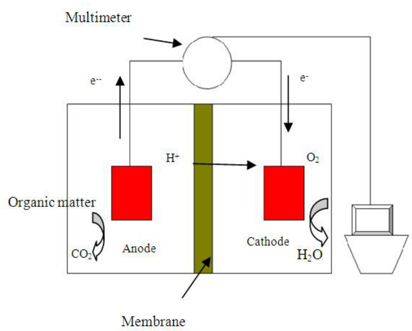

Fig.1. Schematic of a MFC

In one chamber there is microorganisms that produce electrons and protons and in the cathode chamber the reduction process will be happen and MFC produce electricity.

The attachment of microorganisms on electrode surface was shown in Fig.2.

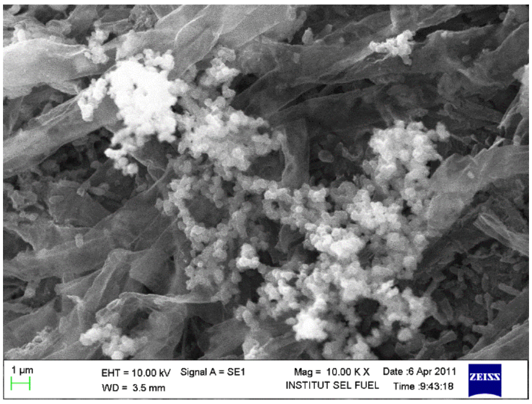

Fig.2. Attachment of microorganisms on electrode surface

As the figure shows the microorganisms very well attached on tle electrode surface. They act as biocatalyst in MFC and convert the organic substrates to electrons and protons. Also they cause some obstacles in MFCs such as biofouling and so on which should be prevented.

The FTIR(Fourier transform infrared spectroscopy) analysis of PEEK and SPEEK was shown in the

Fig.3. as can be seen in the figure, the main difference of

FTIR of PEEK and SPEEK is the broad band of about 3460

cm^{-1} which shows the O-H vibration of sulfonic group. Due

to new substitution upon sulfonation the aromatic C-C

bands can be observed for the PEEK at 1489 cm^{-1}. The

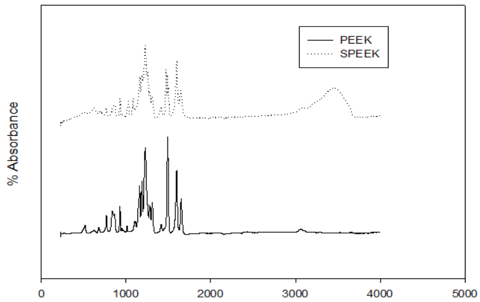

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Fig.3. FTIR of the PEEK and SPEEK

To measure the degree of sulfonation NMR has been used. Also, NMR analysis of the SPEEK is shown in Fig.4. The SPEEK has been prepared in the moderate range , as the DS cannot be controlled exactly and also our previous studies has shown that low or high range of DS sometimes shown unexpected behaviour that could not be predicted [11]. So the DS has been calculated by the formula 1 and which has been sown as above and it was 60%. so this PEM was used with two Nafion membranes (Nafion 112 and Nafion 117) to observe the effect of PEMs in the efficiency of MFCs in wastewater treatment and electricity generation.

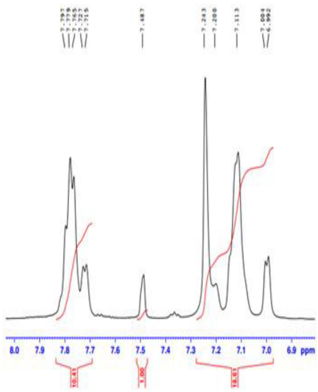

Fig.4. NMR of the SPEEK

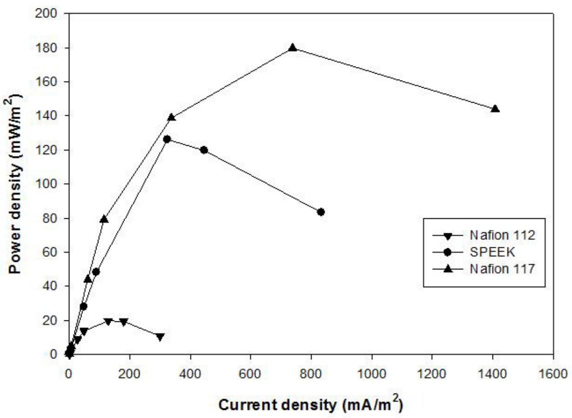

Fig.5. Power density graph

As the Fig.5 shows the maximum power generation of the MFC working with Nafion 117 as PEM is 179.7 mW/m^2 followed by SPEEK which generated the maximum power of 126.1 and the last one is Nafion 112 with 19.7 mW/m^2. As can be seen in all cases Nafion 117 has the highest power production among the studied membranes. It can be due to the great ion exchange properties of Nafion 117 and dense structure of that which block the passing of oxygen from cathode to anode which makes the reaction aerobic and disturb the microorganism's metabolism for electricity production. This obstacle can be seen once Nafion 112 is the separator. Because of thin thickness of the cross section of Nafion 112, most of the oxygen diffuses from cathode to anode and respiration of the substrate is aerobic. SPEEK also by having so many SO^{3-} groups produced acceptable amount of electricity however still the power production is lower than Nafion 117.

4. conclusion

Three common proton exchange membranes were tested in MFC with different COD artificial wastewater to see the effect of them in power production and wastewater treatment. The results have shown that still Nafion 117 has the highest performance however it has also the highest price and so it's not economical. The SPEEK had acceptable performance while it was lower power output and CE than Nafion 117. It was shown in the COD, of 5000 mg/l. MFC is a good device for wastewater treatment however the amount of produced energy still is very low. Another finding of the paper is that the difference of SPEEK and Nafion 117 is going to be decreased at higher COD and it's a great finding for replacement of other PEM as alternative for Nafion 117 and makes the process more viable. Our next purpose is to simulate it and test in different COD to conclude better.

Acknowledgement

The authors would like express their appreciation for the financial support given for this research by the Universiti Kebangsaan Malaysia (UKM) under research grants DLP-2014-002, GGPM-2013-027.

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